FORM PTO-1390 (Modified) (REV 11-2000) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER	
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U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR)	
10/030987	

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP00/06564	11 JULY 2000	28 JULY 1999

TITLE OF INVENTION

GRAFT POLYMERS AS GAS HYDRATE INHIBITORS

APPLICANT(S) FOR DO/EO/US

Maximilian ANGEL, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include itens (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☐ is attached hereto (required only if not communicated by the International Bureau).
   b. ☒ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☒ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☒ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Notice of Priority / PCT/IB/304 / PCT/IB/308
PTO-1449 / Amended Sheets (pages 12 & 13)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
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24. The following fees are submitted:.		CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :			
☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO	**$1040.00**		
☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO	**$890.00**		
☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	**$740.00**		
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)	**$710.00**		
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)	**$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =		**$890.00**	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).		**$0.00**	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	15 - 20 =	0	x	$18.00	**$0.00**
Independent claims	2 - 3 =	0	x	$84.00	**$0.00**
Multiple Dependent Claims **(check if applicable).**			☐		**$0.00**

TOTAL OF ABOVE CALCULATIONS =	**$890.00**	
☐ Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.	**$0.00**	
SUBTOTAL =	**$890.00**	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +	**$0.00**	
TOTAL NATIONAL FEE =	**$890.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).** ☐	**$0.00**	
TOTAL FEES ENCLOSED =	**$890.00**	
	Amount to be: refunded	$
	charged	$

a. ☒ A check in the amount of **$890.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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REGISTRATION NUMBER

Jan 16 2002
DATE

10/030987
JC13 Rec'd PCT/PTO 16 JAN 2002

Graft polymers as gas hydrate inhibitors

The invention relates to the use of graft polymers as gas hydrate inhibitors.

It is known that gas hydrates, also termed clathrate hydrates, can form under certain conditions in media which comprise gas molecules, such as CO_2 or hydrocarbons, e.g. C_1-C_4-alkanes, and water. These gas hydrates are composed of the gas molecules mentioned surrounded by a "cage" of water molecules. Gas hydrates of this type also occur when water is present in mineral oil mixtures or in natural gas mixtures and, for example during transportation, they can lead to blocking of the pipelines.

To prevent this, gas hydrate inhibitors are added to the mineral oil mixtures or natural gas mixtures.

WO 96/41784 and WO 96/41785 disclose gas hydrate inhibitors composed of a copolymer of N-methyl-N-vinylacetamide (VIMA).

US 5 420 370, US 5 432 292, WO 94/12 761 and WO 95/32 356 disclose polymeric additives for clathrate hydrate inhibition in liquid systems. These have a comonomer with a lactam ring in the polymer.

Polyvinylcaprolactam in particular, and also copolymers of polyvinylcaprolactam with, for example, vinylpyrrolidone, have a cloud point when dissolved in water, i.e. a certain temperature at which the polymer precipitates (inverse solubility). For pure polyvinylcaprolactam this is from about 30 to 35°C. A low cloud point such as this is sometimes disadvantageous for the gas hydrate inhibitor application, since the polymer can precipitate in the gas/oil/water phase which is to be conveyed if the temperature of this phase (i.e. including the water of this phase) is high, as is very likely to occur in practice. Use is therefore widely made of copolymers of vinylcaprolactam with, for example, vinylpyrrolidone, or else with other hydrophilic monomers which raise the cloud point, including, for example, ionic monomers which have ionic groups such as carboxyl, sulfonate or (quaternized) ammonium (WO 96/38492).
WO 96/38492 discloses gas hydrate inhibitors comprising a polymer which has a 3- to 15-membered ring bonded to the polymer via a particular linking unit (spacer).

Graft polymers per se are known from the prior art. For example, the German Patents DBP 1077430, 1081229, 1084917 and 1094457 describe processes for preparing various graft polymers, such as graft polymers of polyvinyl esters or modified polyvinyl alcohols. EP 285 038 discloses the use of graft polymers based on polyalkylene oxides as graying inhibitors. EP 44 995 discloses graft polymers of PVA.

It is an object of the present invention to provide polymers which can be used as gas hydrate inhibitors and can be prepared more cost-effectively and can be varied to meet a variety of industrial requirements. The structure of these polymers must be such that they interact with differing interfaces or surfaces, in particular in complex gas-water mixtures and at a variety of temperatures with the result that no gas hydrates form, and it must be possible to use readily available monomers to build up the polymers.

We have found that this object is achieved by using graft polymers as gas hydrate inhibitors.

The idea of using graft polymers as gas hydrate inhibitors enables individual polymer components, such as the base polymer (also termed the graft base), and the monomers to be grafted on, to be ideally matched to one another as requirements dictate, inter alia in terms of their spatial arrangement.

The graft polymers in their entirety may be water-soluble or merely water-dispersible. As long as a dispersion of the polymers in water can be produced using the usual methods, the graft polymers used may per se also be water-insoluble, but preference is given to water-soluble graft polymers. The graft polymers used according to the invention may also be "comb polymers".

The graft base of the graft polymers may be either a hydrophilic polymer or a hydrophobic polymer, preferably a hydrophilic polymer. Polymers with a hydrophobic part and a hydrophilic part may also be used. There is a wide variety of possible monomers for the units grafted on. It is precisely this variability of the system which is an advantage of the present invention.

The graft polymers may therefore be used with a wide variety of solvents in mixtures for gas hydrate inhibition.

Solvents which may be used for the gas hydrate inhibitors are alcohols, e.g. methanol, isopropanol or butyl glycol, and also ethers, in particular partially etherified glycols, and

synergistic effects are possible with some solvents (see also WO 98/19980). Solvents with a high flashpoint and a low ground water pollution classification, e.g. water or ethylene glycol, are preferred for handling reasons, e.g. to reduce safety risks and for reasons of toxicity.

The possibility of using water is seen as a particular advantage of the use according to the invention of the graft polymers.

However, it is also possible to use ethylene glycol, which is chemically closely related to some preferred graft polymers. Low-molecular-weight polyalkylene glycols, in particular polyethylene glycol, may be added subsequently as solvent (for viscosity reasons). Their advantage is that they have a high flashpoint (about 111°C in the case of ethylene glycol) combined with good aquatic toxicity values.

A polyalkylene glycol (liquid and low-molecular-weight), preferably polyethylene glycol, may even be used as solvent for any organic initiator (organic peroxide) which may be used in preparing the graft polymers, or for monomer which is not liquid at room temperature, for example vinylcaprolactam.

One way of making the graft polymers soluble or at least dispersible in water or in other polar solvents is to use a hydrophilic graft base for the graft polymer. Possible graft bases are polyalkylene glycols, polyvinyl alcohols, polyvinylamides, polyvinylpyrrolidone, polyethers, polyesters, polyurethanes, polyacrylamide, polysaccharides, e.g. starch, alginates, pectins, natural rubbers, caseins, gelatin, cellulose ethers, e.g. methylcellulose, starch ethers, polyalkyleneimines, polycarboxylic acids, polyvinylsulphonic acids or polyvinylphosphonic acids or copolymers of these. Preference is given to polyalkylene glycols, in particular polyethylene glycols, polyethyleneimines, polyvinyl alcohols, polyvinylpyrrolidone and polyvinylamine.

Possible hydrophobic base polymers are: polyalkylene glycols, such as ethylene oxide-propylene oxide copolymers or ethylene oxide-propylene oxide block copolymers, polyethers, poly(meth)acrylates, polyolefins, e.g. polyethylene, polypropylene, polyisobutylene, polybutadiene, polyisoprene, polystyrene and styrene copolymers, polyvinyl acetate, polyvinyl ethers, polyvinyl formals, polyvinyl acetals, polyvinyl chloride or other halogenated polyvinyl compounds, e.g. polyvinylidene chloride, polychloroprene, polytrifluorochloroethylene, polytetrafluoroethylene, polyacrylonitrile, polyamide,

polyurethanes, silicones, polycarbonate, polyterephthalate, cellulose or cellulose esters or polyoxymethylene or copolymers of these.

Certain polymers may, as a result of their composition, have both hydrophilic and hydrophobic character. The skilled worker knows how to select the composition to achieve this in a particular case.

Possible monomers for the units grafted on may be water-soluble or water-insoluble. Preferred monomers are N-vinyllactams, N-vinylamides, in particular N-vinyl-N-methylacetamide, acrylates, acrylamides and/or vinyl esters, preferably N-vinyllactams, in particular N-vinylcaprolactam.

The units grafted on generally make up from 10 to 90% by weight, preferably from 25 to 75% by weight, particularly preferably from 40 to 60% by weight of the graft copolymers.

It is particularly advantageous to use graft polymers which have a hydrophilic base polymer and N-vinyllactams as the unit grafted on.

The invention therefore also provides graft polymers with a graft base of hydrophilic polymers having at least one heteroatom in the main chain and with N-vinylcaprolactam as the unit grafted on, and also, if desired, another monomer mentioned above.

According to the invention preference is given to graft polymers in which the graft base is a polyalkylene glycol, a polyalkyleneimine, a polyether or a polyurethane. Particular preference is given to polyethylene glycol as base polymer and N-vinylcaprolactam or N-vinylcaprolactam/vinyl acetate as monomer grafted on.

The graft polymers used according to the invention can be prepared in a manner known per se, e.g. as described in DE 1 077 430 or 1 084 917.

In these publications a mixture made from monomer(vinyl acetate)/polyalkylene glycol/initiator) is (generally) first prepared. This however, raises fundamental questions regarding safety. The polymerization of a part of the mixture is then begun and the remainder is added via a feed and - if desired with addition of solvent - polymerized to completion.

The process described in EP 0 219 048 (page 2, lines 49 ff.) may also be used. In this, polyalkylene oxide is, for example, the initial charge and monomer (vinyl acetate) and initiator are added all at once, in portions or continuously. Another process suitable for preparing the graft polymers used according to the invention is that described in EP 0 285 038 (polyalkylene oxide, vinylpyrrolidone, vinyl ester).

A preferred way of preparing the graft polymers used according to the invention is to heat the entire amount of, or most of, the base polymer, e.g. polyethylene glycol of molar mass typically from 200 to 40,000 g/mol, preferably from 600 to 10,000 g/mol, particularly preferably from 1500 to 6000 g/mol, in a stirred reactor until it becomes liquid, if appropriate. The monomer, e.g. vinylcaprolactam - if desired mixed with a solvent, e.g. ethylene glycol - and a peroxidic initiator (e.g. tert-butyl 2-ethylperoxihexanoate) - if desired mixed with a solvent, e.g. methanol - are then metered in from separate feeds over a period of several hours while the initial charge is at, for example, 80°C. If the viscosity becomes excessive during the course of the reaction an appropriate amount of a solvent, preferably water or ethylene glycol, may be added. The addition may take place either at an earlier stage prior to the grafting reaction or at the start of this reaction, but preferably at the latest possible juncture during the grafting reaction and ideally not until the grafting reaction is complete. The amount of solvent metered in should be kept as small as possible.

After completion of the reaction polymerization may be continued, e.g. by adding another initiator. The pressure and temperature may be raised for this, if desired.
The finished polymer may be diluted with any desired solvent. It is advisable to dilute with water or ethylene glycol or with a mixture of the two.

In many cases the conversion of the grafting reaction may best be determined indirectly by determining the cloud point of the graft polymer and comparing with an ungrafted polymer. For this the polymer is usually dried and an aqueous solution, for example, is prepared from the dry polymer. The clouding of the solution or, respectively, the precipitation of the polymer as a function of temperature can easily be determined.

The cloud point may be determined to DIN 53 917.

The graft polymers may be used, also in combination with other suitable agents, as gas hydrate inhibitors.

These other agents may be other polymers, such as hydroxyalkylcelluloses, polyvinylpyrrolidone or polyvinylcaprolactam, or else alcohols, such as methanol, ethanol or ethylene glycol, or water-soluble salts, preferably in amounts of from 1 to 3.5% by weight, based on the weight of the entire liquid system.

The invention also provides a process for preventing or reducing the formation of gas hydrates in liquid or gaseous systems, which comprises adding a graft polymer to the liquid systems.

The K values of the graft polymers used according to the invention (determined as described by Fikentscher, Cellulose Chemie, 13, 58-64, 71-74, 1932; 1% strength aqueous solution, 20°C, $K = k \cdot 10^3$) are from 10 to 120, preferably from 15 to 90, in particular from 20 to 60. The molecular weights of the graft polymers (M_w) are from 2000 to 1,000,000, preferably from 500 to 300,000, particularly preferably from 10,000 to 100,000.

The graft polymers which can be used according to the invention as gas hydrate inhibitors may be used either in pure aqueous solution or else in solvent mixtures, e.g. water/alcohol, in particular ethylene glycol. After removal of the solvent and, if desired, drying, the polymers may also be used in powder form. If the graft polymers have hydrophilic character powders of this type can easily be redispersed or, respectively, redissolved for the purposes of the invention at their point of use in media in which water is present and in which gas hydrate tends to form.

The polymers are added to the liquid systems, i.e. to the mineral oil mixtures or natural gas mixtures, in the usual amounts which the skilled worker will adapt to the circumstances of each case.

Examples

Example 1

		g	% by weight	
Initial charge	Pluriol E 6000	300	50	
Feed 1	vinylcaprolactam	150	25	
	vinyl acetate	150	25	
Feed 2	tert-butyl 2-ethyl-peroxyhexanoate (98 % strength)	4	=1.3 %	based on monomers
	methanol	30		
Feed 3	demineralized water	900		

Pluriol E 6000: polyethylene glycol with molecular weight 6000

The initial charge was stirred at 150 rpm in a 2 l HWS mixer under a slow flow of nitrogen and heated to an external temperature of 100°C.

Once the polyethylene glycol with molecular weight 6000 (Pluriol E 6000, BASF AG) in the initial charge had been completely melted, 10% of feed 2 was added to the initial charge and stirred for 5 min. Feeds 1 and 2 were then added dropwise, in each case over a period of 5 h. Once the feeds had been completed polymerization was continued for 3 h. Feed 3 was then added over a period of 30 min, followed by cooling.

Solids content in % by weight: 38.1
K value 21.6 (measured at 1 % strength in ethanol)

Example 2

Preparation as in Example 1, experiment at 100°C external temperature. Cf. Table 1.

Example 3

		g	% by weight	
Initial charge	PTHF 1000 *	180	30	
	Partial quantity of feed 2	7		
Feed 1	vinyl acetate	60	10	
	vinylpyrrolidone	315	52.5	
Feed 2	tert-butyl 2-ethyl-peroxyhexanoate (98 % strength)	4.5	=1.1 %	based on monomers
	methanol	45		
Feed 3	vinylpyrrolidone	45	7.5	
Feed 4	tert-butyl 2-ethyl-peroxyhexanoate (98 % strength)	1.3	=0.3 %	based on monomers
	methanol	13		
Feed 5	demineralized water	880		

* polytetrahydrofuran with molecular weight 1000 (hydrophobic)

The experiment was carried out in a 6 l stirred Juvo reactor. The reactor was pressurized three times with nitrogen at 10 bar. The initial charge with the partial quantity of feed 2 was heated to an internal temperature of about 95°C. At 95°C feeds 1 and 2 were begun. Feed 1 was metered in within a period of 6 h and feed 2 within a period of 8 h. Once feed 1 had been completed feed 3 was metered in within a period of 1.5 h. Once feed 2 had been completed polymerization was continued for 1 h. Feed 4 was metered in over a period of 2 h (still) at 95°C. Once feed 4 had been completed polymerization was continued for a further 3 h at 95°C. Feed 5 was then added over a period of 30 min, followed by cooling.

Example 4

Preparation as in Example 1, experiment at 90°C external temperature. Cf. Table 1.

Example 5

Preparation as in Example 1 (unlike in Example 1 PTHF 250 (polytetrahydrofuran with molecular weight 250, hydrophilic) is a clear solution and requires no melting). Experiment at 100°C external temperature. Cf. Table 1.

Example 6

Preparation as in Example 1, experiment at 80°C external temperature. Cf. Table 1.

Since the experiment gave a very high viscosity after feeds 1 and 2 had been completed, a partial quantity of feed 3 (300 g of water) was added straight away during the further polymerization. The remaining amount of water was added prior to cooling.

Table 1

Compositions for the experiments of the examples

Ex.	Initiator		GB**		VCap	VAc	VP	K value ***	SC
	Type	% by wt.*		% by wt.	% by wt.	% by wt.	% by wt.		% by wt.
1	tBEPHA	1.3	Pluriol E 6000	50	25	25		21.6	38.1
2	tBEPHA	1.6	Pluriol E 6000	60	40			22.8	40.1
3	tBEPHA	1.4	PTHF 1000	30		10	60	22.9	38.5
4	tBPPiv	1.3	Pluriol E 6000	50	40	10		23.9	39.3
5	tBEPHA	1.2	PTHF 250	35	30		35	22.5	40.1
6	tBPPiv	1.4	Pluriol E 6000	50	30		20	26.4	40.4

* based on monomer
** GB = graft base
*** 1% strength in ethanol

% by wt. % by weight

tBEPHA tert-butyl 2-ethylperoxyhexanoate
tBPPiv tert-butyl peroxypivalate
PTHF (250) polytetrahydrofuran (molecular weight)

VCap vinylcaprolactam
VAc vinyl acetate
VP vinylpyrrolidone

SC Solids content

Table 2

Freezing point results (ball stop method) and cloud point (0.5% by weight of polymer in water)

Example	Ball stop °C	Cloud point °C	Comments
Comp. 1	4.0	---	Ball stop zero value (no polymer)
Comp. 2	0.5	32	Vinylcaprolactam homopolymer (K value 20)
Comp. 3	3.0	> 100	Vinylpyrrolidone homopolymer (K value 20)
1	2.0	80	
2	1.5	90	Minimal clouding at 50°C (disappears again)
3	2.5	90	Slight clouding
4	1.5	90	Minimal clouding at 40°C (disappears again)
5	1.0	75	
6	1.5	65	

The freezing point was determined by the "Ball stop method" using a test method similar to that described in Example 1 of WO95/32356.

This method relates to the testing of freezing points of water/THF mixtures resulting from adding a variety of polymers (demonstrating hydrate formation). These are frozen at 0.5% strength in a water/THF (81/19% by weight) mixture.

The following equipment and reagents are needed to determine the freezing point of a variety of polymers/(water/THF) mixtures:

- water/THF mixture (81/19% by weight)
- Julabo F 18 temperature-controlled bath with water/ethylene glycol (5/1) refrigerant mixture
- Multifix Constant stirrer
- holder for test tubes (5 ml)

- small stainless steel balls to improve mixing in the test tube

A 0.5% strength solution of the polymer to be studied was prepared in water/THF (81/19). The test tube was filled to two thirds of its capacity, a small stainless steel ball was added and the tube was sealed and secured in the test-tube holder. The measurement was started at 4°C bath temperature and with a rotation rate of 20 rpm, and the temperature was lowered by 0.5°C hourly until the sample had frozen or, respectively, the steel ball was no longer moving within the test tube, or 0°C had been reached. A blank sample was run in parallel with each measurement.

We claim

1. The use of graft polymers as gas hydrate inhibitors.

2. The use as claimed in claim 1, wherein the graft polymers have a hydrophilic and/or hydrophobic base polymer.

3. The use as claimed in claim 2, wherein the hydrophilic base polymers are polyalkylene glycols, polyvinyl alcohols, polyvinylamides, polyvinylpyrrolidone, polyethers, polyesters, polyurethanes, polyacrylamide, polysaccharides, cellulose ethers, polyalkyleneimines, polycarboxylic acids, polyvinylsulfonic acids or polyvinylphosphonic acids or copolymers of these.

4. The use as claimed in claim 2, wherein the hydrophobic base polymers are polyalkylene glycols, such as ethylene oxide-propylene oxide copolymers or ethylene oxide-propylene oxide block copolymers, polyethers, poly(meth)acrylates, polyolefins, polystyrene or styrene copolymers, polyvinyl acetate, polyvinyl ethers, polyvinyl formals, polyvinyl acetals, polyvinyl chloride or other halogenated polyvinyl compounds, polyacrylonitrile, polyamide, polyurethanes, silicones, polycarbonate, polyterephthalate, cellulose, cellulose ethers or cellulose esters or polyoxymethylene or copolymers of these.

5. The use as claimed in claim 1, wherein the graft polymers contain grafted-on units of water-soluble and/or water-insoluble monomers.

6. The use as claimed in claim 5, wherein the units grafted on make up from 10 to 90% by weight of the graft polymer.

7. The use as claimed in claim 5, wherein the units grafted on comprise N-vinyllactams, N-vinylamides, acrylates, acrylamides and/or vinyl esters.

8. The use as claimed in claim 7, wherein the units grafted on comprise N-vinylcaprolactam.

9. A graft polymer composed of a hydrophilic base polymer having at least one heteroatom in the main chain and of N-vinyllactams and also, if desired, of a grafted-on unit

comprising another monomer as claimed in claim 7, although polyphenylene ether shall be excluded as a base polymer.

10. A graft polymer as claimed in claim 9, wherein the hydrophilic base polymer is a polyalkylene glycol, a polyalkyleneimine, a polyether or a polyurethane, although polyphenylene ether shall be excluded as a base polymer.

11. A graft polymer as claimed in claim 10, wherein the hydrophilic polymer is polyethylene glycol.

12. A graft polymer as claimed in claim 9, wherein the unit grafted on is N-vinylcaprolactam or else, if desired, a vinyl ester.

13. A process for preventing or reducing the formation of gas hydrates in liquid or gaseous systems, which comprises adding a graft polymer to the liquid or gaseous systems.

Graft polymers as gas hydrate inhibitors

Abstract

Graft polymers are used as gas hydrate inhibitors.

Declaration, Power of Attorney and Petition

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

GRAFT POLYMERS AS GAS HYDRATE INHIBITORS

the specification of which

[ ] is attached hereto.

[ ] was filed on _____ as

Application Serial No. _____

and amended on _____.

[x] was filed as PCT international application

Number *PCT/EP/00/06564*

on *11 July 2000*,

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed	
19935063.9	*Germany*	*28 July 1999*	[x] Yes	[ ] No

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	**Filing Date**	**Status (pending, patented, abandoned)**

And we (I) hereby appoint: Norman F. Oblon, Reg. No. 24,618; Marvin J. Spivak, Reg. No. 24,913; C. Irvin McClelland, Reg. No. 21,124; Gregory J. Maier, Reg. No. 25,599; Arthur I. Neustadt, Reg. No. 24,854; Richard D. Kelly, Reg. No. 27,757; James D. Hamilton, Reg. No. 28,421; Eckhard H. Kuesters, Reg. No. 28,870; Robert T. Pous, Reg. No. 29,099; Charles L. Gholz, Reg. No. 26,395; William E. Beaumont, Reg. No. 30,996; Jean-Paul Lavalleye, Reg. No. 31,451; Stephen G. Baxter, Reg. No. 32,884; Richard L. Treanor, Reg. No. 36,379; Steven P. Weihrouch, Reg. No. 32,829; John T. Goolkasian, Reg. No. 26,142; Richard L. Chinn, Reg. No. 34,305; Steven E. Lipman, Reg. No 30,011; Carl E. Schlier, Reg. No. 34,426; James J. Kulbaski, Reg. No. 34,648; Richard A. Neifeld, Reg. No. 35,299; J. Derek Mason, Reg. No. 35,270; Surinder Sachar, Reg. No. 34,423; Christina M. Gadiano, Reg. No. 37,628; Jeffrey B. McIntyre, Reg. No. 36,867; William T. Enos, Reg. No. 33,128; Michael E. McCabe, Jr., Reg. No. 37,182; Bradley D. Lytle, Reg. No. 40,073; and Michael R. Casey, Reg. No. 40,294; our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of **OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P. C.**, whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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